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Photochromism based on reversible proton transfer

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ABSTRACT

Photochromism based on reversible proton transfer between metastable-state photoacids and acidochromic dyes is studied. Metastable-state photoacids reversibly produce a large proton concentration under moderate irradiation, protonate the acidochromic dyes and induce color change. This mechanism is different from that of conventional photochromic materials based on photoinduced structural change. The color change and the stimulating wavelength can be controlled by choosing different acidochromic dyes and photoacids. Reversible changes of various colors under sunshine or visible lights of different wavelengths were demonstrated in both solutions and polymer matrix.

1. Introduction

Photochromic materials that change their colors upon irradiation have been studied for decades [1–9]. These materials undergo a reversible photoreaction and transform to a structure with a different color. The photochromic behavior of a material is often characterized by the color without irradiation, the color upon irradiation, and the irradiation wavelength. Common photochromic molecules such as spiropyrans, diaryethenes and azobenzenes have colorless or light colored forms that respond to UV light and change to colorful forms. Some highly conjugated ones and some negative photochromic molecules can be activated by visible light and change from colorful forms to colorless forms [10–12]. Spiropyrans have also been utilized to control proton transfer with light [13–15]. In this work, we studied a different photochromic mechanism based on reversible proton transfer, and demonstrated its advantages in the design of photochromic materials.

Changes of optical properties (UV–vis absorption, fluorescence etc.) caused by photo-induced protonation have been reported by several groups [16–20]. Photoacid generators (PAGs) were used to produce a large proton concentration, which irreversibly changed the optical properties of the materials. Irreversible photo-induced color change is not generally considered as photochromism. Metastable-state photoacids can reversibly change pH over two units upon irradiation [21–23]. In addition, they can work under visible light with moderate intensity, e.g., sunlight and LED light, which is highly desirable for various applications. In this work, composites of metastable-state photoacids and acidochromic dyes were studied. Upon irradiation, the acidity increase of the photoacid induced protonation of the acidochromic dyes and consequent color change. In the absence of the activating light, the photoacid returned to the low acidity state, took back the proton from the dye, and the color changed back. This mechanism allows one to design a certain color change and choose a desirable stimulating wavelength by selecting different photoacids and dyes. Demonstrations of this advantage are described below.

2. Results and discussion

Compound **1** (Scheme 1) is a well-studied metastable-state photoacid [21,22]. It can reversibly change pH of an aqueous solution by more than 2 units under blue light. Compound **1** was mixed with an acidochromic dye **2** in 95% ethanol forming a photochromic solution. The dye **2** was synthesized following a literature method [24]. It has a pK_a of about 4.7 which is in the range of the pH change of **1**. It has a yellow color similar to that of **1**, which means the color before irradiation is not affected by the ratio of the two components. In an acidic condition, **2** is protonated and becomes blue. Blue and yellow are complimentary colors, and thus have maximum color contrast.

An ethanol solution of **1** and **2** was irradiated with a 470 nm blue LED light (photon flux ~1000 μmol m^2 s^{-1}). Detailed procedure is given in the Section 4. The color quickly changed from yellow to blue upon irradiation in about 2 min (Fig. 1). Before irradiation, UV–vis spectrum showed a strong absorption at

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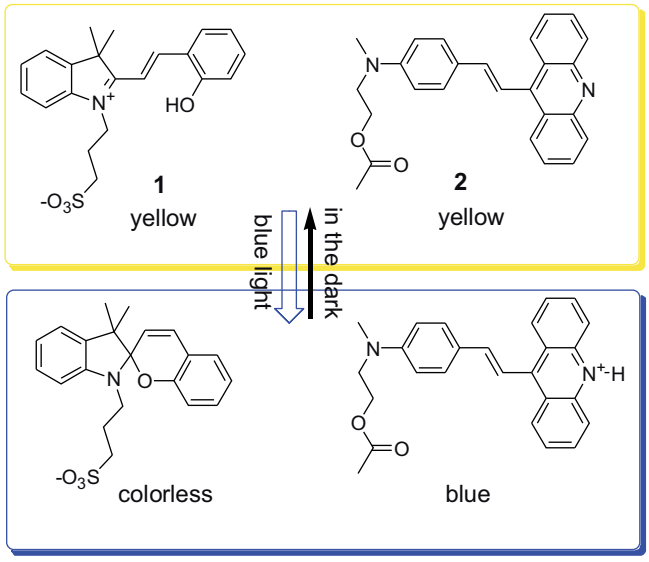

Scheme 1. Photochromism of photoacid **1** and dye **2**.

440 nm, which is an overlap of the absorption of **1** and **2**. After irradiation, this absorption decreased and an absorption at 604 nm appeared. The absorption at 604 nm is due to the formation of the protonated dye **2**, which gives the blue color. In the dark or dim indoor light, the blue solution changes back to yellow in about an hour. The slow recover of the yellow color is mostly due to the slow reverse process of the photoacid **1**, which is the process from the photo-induced high-acidity state to the low-acidity state in the dark [21]. It can be improved by using a media with higher hydrogen-bond donor (HBD) acidity (Taft–Kamlet α scale) as described below [21], or a different photoacid with a faster reverse rate, which is currently investigated by our group.

It is important to load the photochromic composite to polymer materials for different applications. Therefore, thin films of polycaprolactone loaded with **1** and **2** were prepared by spin casting. The weight percentage of **1** and **2** are both 5%. In addition, 5 wt% of triethylene glycol was added to improve proton transfer in the polymer. Upon irradiation, the greenish yellow thin film changed to greenish blue (Fig. 1). UV–vis spectrum of the thin film showed the decrease of absorption at about 420 nm, and increase of the absorption at 590 nm. In about 10 h after irradiation, the UV–vis spectrum changed back to the one before irradiation and so was the color of the film.

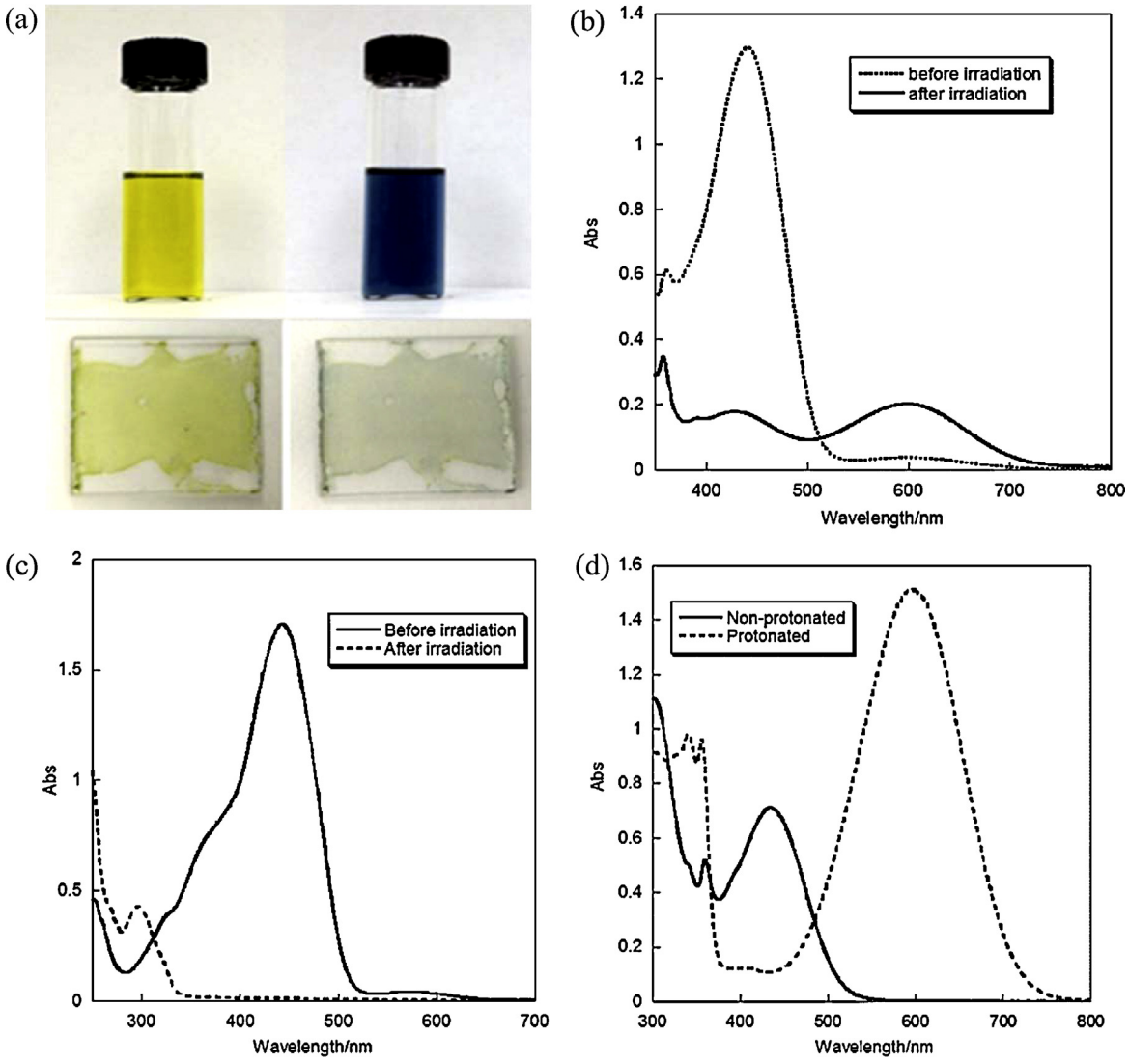

Fig. 1. (a) Color change of a solution and a PCL film of **1** and **2**, (b) UV–vis spectra of a diluted solution of **1** and **2** in 95% ethanol before and after irradiation, (c) a solution of **1** before and after irradiation, and (d) a solution of **2** before and after protonation with HCl.